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LNP* Specialty Compounds

Thermal and environmental resistance of glass-reinforced thermoplastics

Sharing our futures

Thermal endurance

It’s common knowledge that glass reinforcement increases room-temperature mechanical properties of thermoplastics by a factor of two or more. But what amount of this increase is maintained after heat-aging the reinforced compounds? Or after exposing them to various chemicals? Here are new data to answer these questions.

Strength, stiffness and other mechanical properties of almost all thermoplastics can be doubled and even tripled by proper incorporation of fillers and reinforcement. Short-term high-temperature performance, commonly measured by deflection temperature, is also greatly increased by fiber reinforcement. These performance advantages, coupled with the economies and advantages of injection-molding production, have opened many new application areas for thermoplastics.

The increased use of thermoplastic composites in high-temperature, high-performance applications has, in turn, generated the need to evaluate their long-term performance reliability. This is determined by testing how long a product made from a thermoplastic composite will retain its properties, and by establishing the highest practical continuous-use temperature for the material. Properties usually tested are tensile strength, tensile impact strength and dielectric strength.

Thermal endurance

The most widely accepted means of establishing thermal endurance of a polymer is that used by Underwriters’ Laboratories to determine the temperature index (continuous-use temperature rating) of a plastic material (UL746B). This test procedure is based on the fact that a linear time-temperature relationship exists for the aging of a thermoplastic polymer; that is, thermal degradation obeys the Arrhenius reaction-rate equation. The UL test procedure for glass-fortified thermoplastics consists of these steps

- A polymer is aged at two or more different test temperatures.
- Reduction of properties caused by thermal degradation is monitored periodically to generate property-degradation curves such as those shown in figure 1.
- The time at each test temperature, that reduces a physical property to 50% of its original value is then plotted, and an Arrhenius curve is fitted to the data points by regression analysis, as shown in figure 2 (data from figure 1b).

A control material with a known index is run concurrently with the new polymer being indexed to eliminate effects of test variability. The control material for glass fiber reinforced composites is normally the base resin.

Figure 1a
Heat-stabilized nylon 6/6

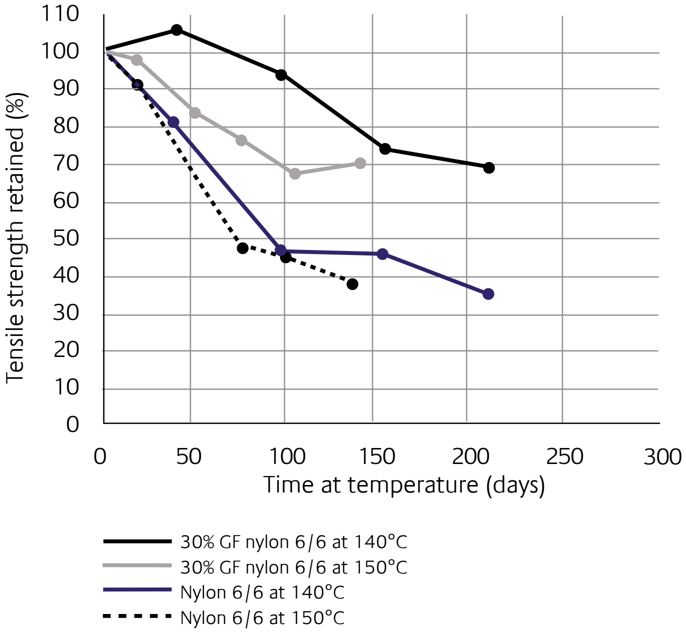


Figure 1b
Heat-stabilized nylon 6/6

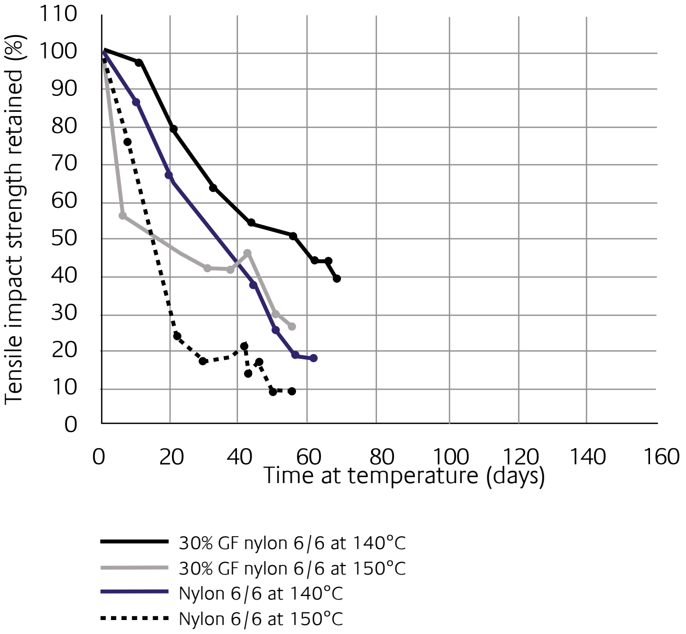


Figure 1c
Polycarbonate

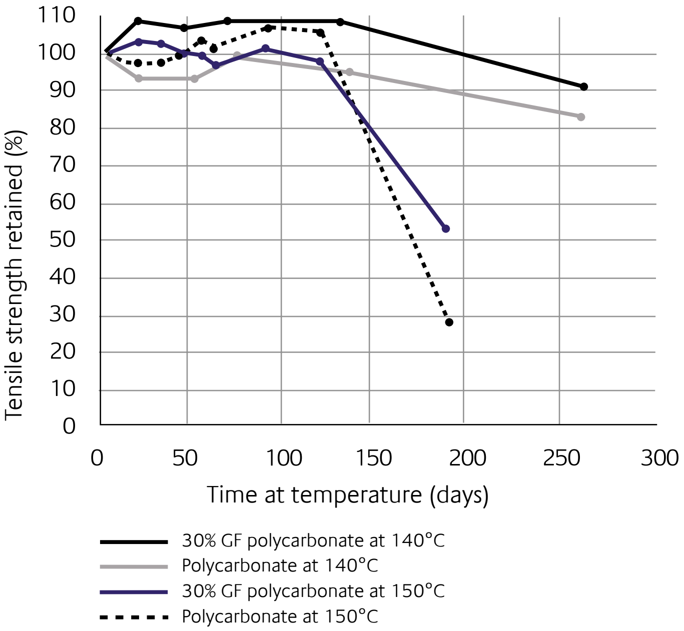


Figure 1d
Polycarbonate

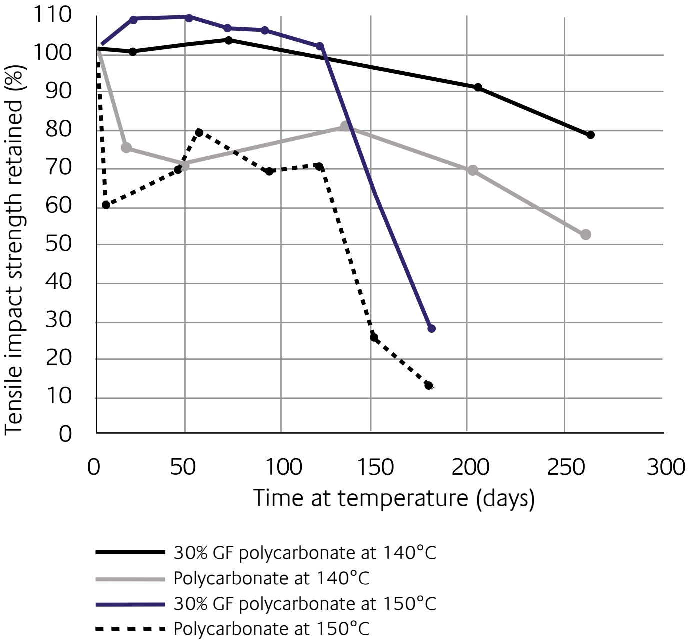


Figure 1e
Polysulfone

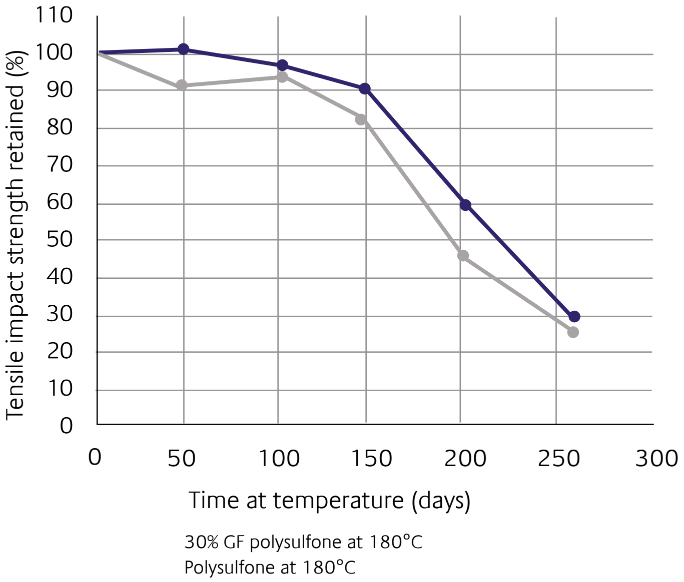
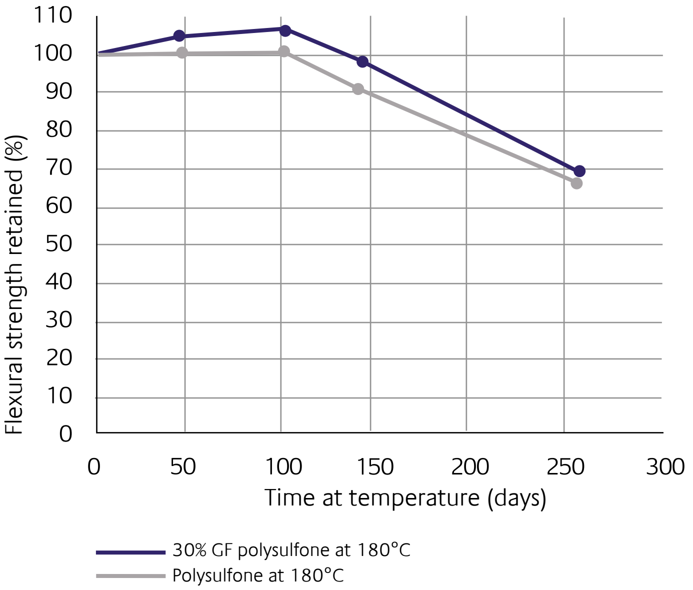
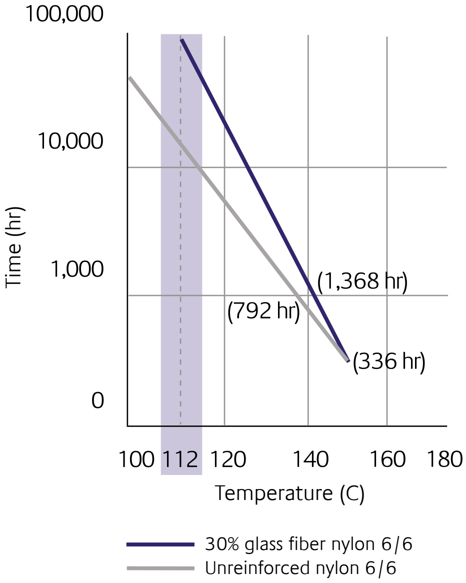


Figure 1f
Polysulfone



The Arrhenius curve generated by this procedure can be used to predict the property half-life of the polymer at a given temperature. The UL temperature index, or continuous-use temperature, is determined by the interrelationship of the curves for the control and for the composite being indexed. Generally, the continuous-use temperature can be determined by dropping a vertical line from the intersection of the 100,000-hr line and the Arrhenius curve (see figure 2). Since most applications are designed with a safety factor (on life) of 2, a part molded from an indexed compound will still meet minimum requirements of the application after 100,000 hr exposure at the rated temperature.

Figure 2
Time-temperature relationships for tensile impact strength of heat-stabilized reinforced (30% glass) and unreinforced nylon 6/6



Studies of thermal degradation indicate that property reduction is primarily caused by free radical chain scission and crosslinking of the polymer molecules close to the surface. This mechanism produces a low-molecular-weight resin on the surface of the part, which embrittles and weakens the polymer or polymer composite.

Tensile impact strength of the resin is affected most by this phenomenon, and this property usually reaches half-life before any other property. The temperature index assigned to a compound is generally controlled by tensile impact strength. Higher temperature indexes may be acceptable if the material is to be used in applications where impact strength is not critical.

The thermal-degradation curves of figure 1 were generated on 30% glass fiber reinforced composites of nylon 6/6, polycarbonate, and polysulfone; the base resin of each compound was used for the control. In all cases, the curves for the composites lie above those for the base resin, indicating that glass reinforcement does not accelerate polymer degradation, and that the glass/resin composite retains a greater percentage of the original property, at a given time and temperature, than does the unreinforced base resin.

Based on these data, UL has issued a temperature index of 105°C for LNP*’s 30% glass-reinforced, heat-stabilized type 6/6 nylon. Although Arrhenius curves for glass-reinforced polycarbonate and polysulfone have not been plotted (testing has not yet been completed), it is apparent from the thermal-degradation curves that the property half-life of the glass-reinforced composites is at least equal to that of the unreinforced base resin.

Chemical resistance

Eighteen polymers and polymer composites were compared in a number of chemical environments under conditions typically encountered by molded products. The resulting data show that glass fiber reinforced thermoplastic resins have better chemical resistance than their unreinforced base resins. Trends are established that can be used to predict chemical resistance of composites and polymers in other environments.

One difficulty encountered in a chemical-resistance testing program is that of establishing meaningful test parameters. In this study, changes in tensile strength of both unstrained and strained samples at room temperature and at elevated temperature were defined as the most important parameters for study. Data from the tests are summarized in tables 1 and 2.

If a polymer or polymer composite is observed to have less than 3% loss in tensile strength it is judged excellent (E). Within experimental accuracy, no significant change in the strength of the polymer is apparent. In some cases, an actual increase in tensile strength is observed, attributable in part to stress relief. The number of test bars exhibiting tensile strength gain was much lower in specimens that were strained. Materials with a tensile-strength loss between 3% and 10% are judged acceptable (A). In most applications, the chemical resistance of polymers for which losses between 10% and 25% are observed is judged fair (F). Long-range resistance properties for this category are minimal, but short-range resistance properties are sufficient to allow exposure during fabrication or other one-time operations. Materials with a tensile-strength loss over 25% are considered unacceptable (X) for contact with the environment indicated, regardless of length of exposure.

Obviously, the closer the parameter studied applies to a field situation, the more useful the data. Inspection of these data, however, shows general trends or profiles. For example, while 30% glass fiber reinforced polyethylene retains tensile strength — strained and unstrained — at elevated temperature in 10% aqueous hydrochloric acid and sulfuric acid solutions, 30% glass fiber reinforced nylon 6 loses over 50% of its tensile strength.

Because most glass fiber reinforced thermoplastics are used at normal ambient temperatures, the room temperature data for tensile-strength change provide a basis for analysis of chemical resistance at “average” conditions. If the application requires only that the thermoplastic be self-supporting, the data for unstrained tensile change should be consulted. The data on tensile-strength change for samples at 0.25% strain offer more utility for most engineering applications.

In addition to the larger losses in tensile strength of strained specimens, other, more specific trends can be observed. If the chemical resistance of a material is judged excellent or acceptable when unstrained, the additional tensile strength loss for the material under strain is generally from 0 to 5%. Thus, most of the glass fiber reinforced thermoplastics judged excellent or acceptable unstrained remain excellent or acceptable strained. On the other hand, thermoplastics with marginal or unacceptable resistance generally lose an additional 5 to 15% of tensile strength when strained. For example, 30% glass fiber reinforced ABS has excellent resistance to ethylene glycol unstrained; the observed value of tensile strength is 19,080 psi. Subjected to 0.25% strain, a 5% additional loss, to 18,070 psi, is observed. The same compound is judged unacceptable in methanol, with a tensile strength of 13,360 psi. Subjected to 0.25% strain, the additional loss is nearly 50% to 7,600 psi.

The effects of a chemical environment are of two general types, solvent effects and degradative effects. Careful attention to the parameters associated with solvation, analysis of empirical results of tests, and regard for special degradative effects observed can result in meaningful predictions of polymer and composite chemical resistance. Degradative effects of chemical environments encountered in normal product service are the exception rather than the rule. The primary effect of most chemical environments on polymers or composites is through their action as a solvent. Solvent effects are functions of polarity and viscosity (consideration must also be made of melting and boiling temperatures). If the polarity of a solvent matches that of a primary polymer bond, the loss in mechanical properties is greater than in other solvents. Thus, a close match represents an incompatible service environment for a given polymer. Selection of a polymer for a given environment should be made by choosing the material farthest from a polarity match with the solvent environment. Thus, inspection of table 3 indicates that glass fiber reinforced nylon 6/6 is resistant to typical cleaning solvents such as carbon tetrachloride, and that glass fiber reinforced polystyrene is unsuitable for exposure to antifreeze (ethylene glycol). Methanol (wood alcohol) of similar polarity but reduced viscosity would be expected to have even a greater deleterious effect on the styrene material. Both of these conclusions are supported in tables 1 and 2.

Another point of interest is that a pure solvent generally has less effect on a polymer or composite than an impure solvent or mixture of solvents. Gasoline, for example, has a greater effect than hexane.

In almost all cases, glass fiber reinforced thermoplastic resins have greater chemical resistance than the unreinforced polymer. Initially, mechanical properties of composites far exceed those of the unreinforced polymer. Thus, even if percent losses in strength were equivalent, the composite would still have greater strength after exposure. Percent strength losses of the composites are generally less than those of the unreinforced polymer.

Composites that are closest to optimum theoretical reinforcement have the best chemical resistance. Production of such composites involves the physiochemical linking of the polymer to the glass fibers. Thus, the resin is tightly bonded in a matrix which does not allow interpenetration of a solvent that could associate more strongly with the resin than the resin associates with the glass.

ASTM D 1822 type tensile impact samples were used for this study. For each chemical environment, five bars were tested. A control sample of equal number was tested and tensile strength calculated. At the end of one week (168 ± 1 hr) at 23 ± 2 deg C, the test bars were removed from the chemical environment. Excess liquid was wiped from the specimens, and they were weighed and tested within 2 hr of removal. Values on strained samples were obtained by positioning the same type of bars in an arced jig which applied 0.25% flexural strain. These samples were immersed and removed from the chemical environment with the unstrained samples.

Elevated temperature chemical resistance was obtained by immersing unstrained test bars in the various environments at 81 ± 2 deg C for 72 ± 1/2 hr. If the boiling point of the solvent was below 81 deg C, the test was run at its boiling point.

Table 1 Chemical resistance of glass fiber reinforced thermoplastics at 23°C for 168 hours

Base resin	Glass filler level weight %	Volume %		Hydrochloric acid (10%)	Sulfuric acid (10%)	Acetic acid	Ammonium hydroxide	Heptane	Ethylene glycol	Methanol	Linseed oil
ABS	30	14.9	unstrained	F	A	A	F	F	E	X	E
			0.25% strain	F	F	F	X	A	A	X	F
SAN	30	15.4	unstrained	F	F	F	X	E	E	X	E
			0.25% strain	F	F	F	F	E	F	X	E
Polystyrene	30	15.0	unstrained	X	X	X	X	A	A	X	F
			0.25% strain	A	X	X	X	X	F	X	F
Polycarbonate	30	16.8	unstrained	A	F	A	X	A	E	F	A
			0.25% strain	A	A	A	X	A	F	F	A
	0	0.0	unstrained	A	A	A	X	F	F	A	A
			0.25% strain	F	F	A	X	A	A	A	F
Polyethylene	30	13.9	unstrained	F	F	F	X	F	E	A	A
			0.25% strain	F	F	F	X	X	A	F	A
Polysulfone	30	17.3	unstrained	F	F	A	F	A	F	A	A
			0.25% strain	X	F	F	F	A	E	A	F
Acetal	30	19.2	unstrained	F	F	F	F	E	F	F	E
			0.25% strain	F	X	F	X	A	A	F	A
	0	0.0	unstrained	E	X	E	E	E	E	E	E
			0.25% strain	E	X	E	E	E	E	E	E
Polypropylene	30	13.2	unstrained	A	A	A	A	X	E	E	E
			0.25% strain	F	A	A	A	X	E	A	A
Nylon 6	30	16.1	unstrained	X	X	X	X	A	E	F	E
			0.25% strain	X	X	X	X	E	E	E	E
Nylon 6/10	30	15.4	unstrained	F	F	F	F	E	E	X	E
			0.25% strain	F	F	F	F	E	E	X	E
Nylon 6/6	30	16.1	unstrained	X	X	X	X	A	F	X	F
			0.25% strain	X	X	X	X	F	F	X	F
	0	0.0	unstrained	X	X	X	X	X	X	X	X
			0.25% strain	X	X	X	X	F	X	X	X
Thermoplastic polyurethane	30	17.4	unstrained	F	F	F	F	E	E	X	A
			0.25% strain	F	F	F	F	E	E	X	A
Thermoplastic polyester	30	18.8	unstrained	A	F	A	F	E	A	E	E
			0.25% strain	A	F	A	F	E	F	A	A
Modified PPO	30	15.2	unstrained	E	A	A	E	F	E	E	E
			0.25% strain	E	A	A	E	A	E	E	F

Table 2 Chemical resistance of glass fiber reinforced thermoplastics at 81°C for 72 hours

Base resin	Glass filler level weight %		Hydrochloric acid (10%)	Ammonium hydroxide (10%)	Ethylene	Methanol	Linseed oil	Sodium hypochlorite solution (Bleach)	Cascade (10%)
ABS	30	unstrained	F	X	F	X	F	X	X
Polystyrene	30	unstrained	F	X	F	X	X	F	X
Polycarbonate	30	unstrained	F	X	A	X	F	A	F
	0	unstrained	A	X	F	F	F	F	F
Polyethylene	30	unstrained	F	X	A	F	F	F	A
Polysulfone	30	unstrained	F	F	F	F	F	A	F
Acetal	30	unstrained	X	F	F	F	A	F	F
	0	unstrained	X	E	E	E	E	A	E
Polypropylene	30	unstrained	F	F	A	F	F	F	A
Nylon 6/10	30	unstrained	X	X	X	X	A	X	X
Nylon 6/6	30	unstrained	X	X	X	X	F	X	X
	0	unstrained	X	X	X	X	X	X	X
Modified PPO	30	unstrained	E	A	E	E	E	E	A

Key
E Excellent — 0 to 3% loss in tensile strength
A Acceptable — 3 to 5% loss in tensile strength
F Fair — 10 to 25% loss in tensile strength
X Not recommended — more than 25% loss in tensile strength

Table 1 continued chemical resistance of glass fiber reinforced thermoplastics at 23°C for 168 hours

Base resin	Glass filler level weight %	Volume %		Corn oil	Sodium hypochlorite solution (bleach)	Kester #1544 flux	Lestoil (2%)	Gasoline	Motor oil	Brake fluid
ABS	30	14.9	unstrained	A	A	A	F	X	F	X
			0.25% strain	F	F	F	X	X	F	X
SAN	30	15.4	unstrained	E	F	A	F	X	X	X
			0.25% strain	E	F	F	X	X	F	X
Polystyrene	30	15.0	unstrained	A	F	A	X	X	F	F
			0.25% strain	A	X	F	X	X	X	X
Polycarbonate	30	16.8	unstrained	E	A	A	F	F	F	F
			0.25% strain	F	F	A	F	F	F	X
	0	0.0	unstrained	A	A	A	E	F	F	F
			0.25% strain	A	A	E	E	X	F	X
Polyethylene	30	13.9	unstrained	A	F	A	X	F	E	A
			0.25% strain	A	F	F	X	X	E	A
Polysulfone	30	17.3	unstrained	A	F	E	F	X	E	X
			0.25% strain	A	F	A	X	X	E	X
Acetal	30	19.2	unstrained	E	F	A	F	F	F	F
			0.25% strain	A	F	E	F	E	E	E
	0	0.0	unstrained	E	E	E	E	E	E	E
			0.25% strain	E	E	E	E	E	E	E
Polypropylene	30	13.2	unstrained	A	F	E	X	X	A	A
			0.25% strain	E	F	A	X	A	A	E
Nylon 6	30	16.1	unstrained	E	X	F	X	F	A	A
			0.25% strain	E	X	F	X	F	A	A
Nylon 6/10	30	15.4	unstrained	A	F	F	F	F	F	A
			0.25% strain	E	F	F	F	F	F	A
Nylon 6/6	30	16.1	unstrained	F	X	F	X	F	F	F
			0.25% strain	F	X	X	X	X	A	A
	0	0.0	unstrained	X	X	X	X	F	F	F
			0.25% strain	X	X	X	X	X	A	A
Thermoplastic polyurethane	30	17.4	unstrained	E	F	X	F	X	F	X
			0.25% strain	E	F	X	X	X	F	X
Thermoplastic polyester	30	18.8	unstrained	A	A	A	F	A	E	E
			0.25% strain	E	A	E	F	A	E	A
Modified PPO	30	15.2	unstrained	A	E	E	X	X	E	E
			0.25% strain	F	E	E	X	X	E	F

Table 2 continued chemical resistance of glass fiber reinforced thermoplastics at 81°C for 72 hours

Base resin	Glass filler level weight %		Gasoline	Motor oil	Brake fluid	Carbon tetrachloride	Benzene
ABS	30	unstrained	X	F	X	X	X
Polystyrene	30	unstrained	X	F	X	X	X
Polycarbonate	30	unstrained	F	E	X	F	X
	0	unstrained	X	A	X	X	X
Polyethylene	30	unstrained	X	A	A	X	F
Polysulfone	30	unstrained	X	E	X	X	X
Acetal	30	unstrained	F	F	F	F	X
	0	unstrained	E	E	E	E	E
Polypropylene	30	unstrained	X	F	X	X	X
Nylon 6/10	30	unstrained	A	A	A	E	A
Nylon 6/6	30	unstrained	F	F	F	A	F
	0	unstrained	F	F	X	E	F
Modified PPO	30	unstrained	X	A	E	X	X

Key
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A Acceptable — 3 to 5% loss in tensile strength
F Fair — 10 to 25% loss in tensile strength
X Not recommended — more than 25% loss in tensile strength

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